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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SHADING DYES

(57) Abstract: The present invention concerns the use of anthraquinone dyes for shading textiles.

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SHADING DYES

FIELD OF INVENTION

The present invention relates to the use of shading dyes in laundry treatment compositions.

BACKGROUND OF INVENTION

A variety of dye types may be used for shading applications in laundry products. For example, direct and acid dyes may be used, and the chromophore may be chosen from triphenyl methane, azo and anthraquinone moieties. Shading benefits function by providing a low level of colour to the white cloth, generally, blue or violet, that enhances the human perception of whiteness.

United States Patent 3748093, to Colgate, discloses the use of Acid blue 205 as a shading dye. Acid blue 205 when used as a shading dye gives a high deposition to nylon. Some acid anthraquinone dyes such as acid blue 80 are used to colour laundry detergent products but lack substantivity to fabric such as cotton.

WO05/003275 demonstrates that some acid dyes have the advantage of depositing to cotton but not building up on cotton over multiple washes. If a build up occurs an unacceptably high level of colour accrues on the cotton. Domestic washes contain a mixture of fabric types and in the application of acid shading dyes care must be taken that build up does not occur on fabric types other than cotton. For acid dyes particular attention must be paid to nylon, as acid dyes are widely used to dye nylon. Anthraquinone dyes

show particular utility in dying nylon. Hence it would be expected that anthraquinone dyes would deposit more to nylon fabrics than to cotton fabrics, where they will build up over multiple washes.

SUMMARY OF INVENTION

We have found that selected dyes are particularly suitable for use in laundry treatment compositions. Contrary to the expectation that selected anthraquinone dyes would build up on nylon this is now shown not to be true.

It is also shown that anthraquinone dyes have the desirable property of not fading rapidly when exposed to light, so that the whiteness benefit is not lost during a day, or days. The anthraquinone dyes are also shown to be more stable than azo, or triphenyl methane dyes. This means that the benefit may be enjoyed through out a day, or days of wearing.

In one aspect the present invention provides a laundry treatment composition comprising from 2 to 60 wt % of a surfactant and from 0.0001 to 0.02 wt % of a dye selected from acid blue 62, 40 and 290.

In another aspect of the present invention is provided a method of treating a textile with an aqueous solution of the laundry treatment composition.

DETAILED DESCRIPTION OF THE INVENTION

Because the dyes are substantive, only a small amount is required to provide the enhanced whiteness effect hence the

treatment composition comprises from 0.0001 to 0.02 wt%, preferably from 0.0005 to 0.01 wt% of the dye, more preferably from 0.001 to 0.01 wt%. Notwithstanding the above, the composition should be such that a "unit dose" provides a suitable dose in solution that is within the thresholds given for the method described below. A "unit dose" as used herein is a particular amount of the laundry composition used for a type of wash. The unit dose may be in the form of a defined volume of powder, granules or tablet.

The method of the present invention employs the dye preferably at a concentration in the range from 10ppb to 1 ppm, most preferably from 100ppb to 500ppb. The low concentration used is such that the dye is at such a level that the dye provides a subtle shade to a fabric rather than what would be perceived by the public as a distinct colour change.

It is preferred that the ionic strength of the aqueous laundry treatment composition is between 0.001 to 0.5, more preferably between 0.02 to 0.2. It is preferred that this ionic strength is provided by dissolution of a "unit dose" of the laundry treatment composition.

The aqueous laundry treatment composition preferably has a pH in the range from 7 to 12, most preferably from 8 to 11. The aqueous laundry treatment composition preferably has a and a surfactant present at a level in the range from 0.1 g/L to 4g/L, most preferably from 0.25 to 2.5g/L. It is preferred that this pH and surfactant level is provided by

dissolution of a "unit dose" of the laundry treatment composition.

BALANCE CARRIERS AND ADJUNCT INGREDIENTS

The laundry treatment composition in addition to the anthaquinone dye comprises the balance carriers and adjunct ingredients to 100 wt % of the composition.

These may be surfactants, builders, foam agents, anti-foam agents, solvents, and enzymes. The use and amounts of these components are such that the composition performs depending upon economics, environmental factors and use of the composition.

The composition may comprise a surfactant and optionally other conventional detergent ingredients. The composition may also comprise an enzymatic detergent composition which comprises from 0.1 to 50 % by weight, based on the total detergent composition, of one or more surfactants. This surfactant system may in turn comprise 0 to 95 % by weight of one or more anionic surfactants and 5 to 100 % by weight of one or more nonionic surfactants. The surfactant system may additionally contain amphoteric or zwitterionic detergent compounds, but this in not normally desired owing to their relatively high cost. The enzymatic detergent composition according to the invention will generally be used as a dilution in water of about 0.05 to 2%.

It is preferred that the composition comprises between 2 to 60 wt % of a surfactant. In general, the nonionic and anionic surfactants of the surfactant system may be chosen

from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.

Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are C_6-C_{22} alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C_8-C_{18} primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO.

Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C_8-C_{18} alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C_9-C_{20} benzene sulphonates, particularly sodium linear secondary alkyl C_{10}-C_{15} benzene sulphonates; and sodium alkyl

glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The preferred anionic detergent compounds are sodium C_{11}-C_{15} alkyl benzene sulphonates and sodium C_{12}-C_{18} alkyl sulphates. Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides.

Preferred surfactant systems are mixtures of anionic with nonionic detergent active materials, in particular the groups and examples of anionic and nonionic surfactants pointed out in EP-A-346 995 (Unilever). Especially preferred is surfactant system that is a mixture of an alkali metal salt of a C_{16}-C_{18} primary alcohol sulphate together with a C_{12}-C_{15} primary alcohol 3-7 EO ethoxylate.

The nonionic detergent is preferably present in amounts greater than 10%, e.g. 25-90% by weight of the surfactant system. Anionic surfactants can be present for example in amounts in the range from about 5% to about 40% by weight of the surfactant system.

BLEACHING SPECIES

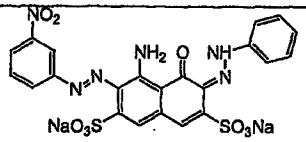
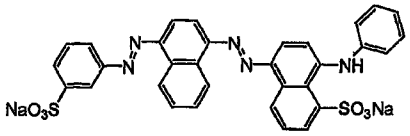
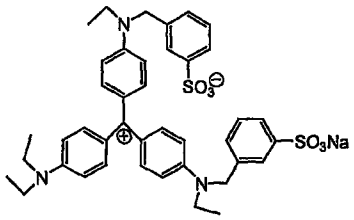
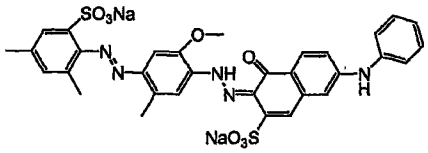
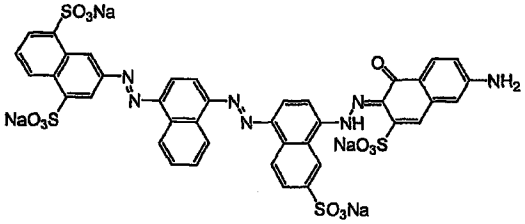
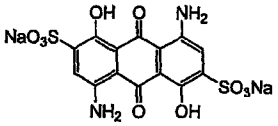
The laundry treatment composition may comprise bleaching species. The bleaching species, for example, may selected from perborate and percarbonate. These peroxyl species may be further enhanced by the use of an activator, for example, TAED or SNOBS. Alternatively or in addition to, a transition metal catalyst may used with the peroxyl species.

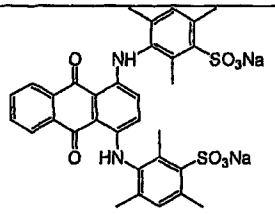
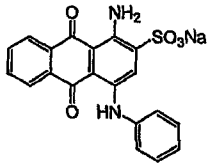
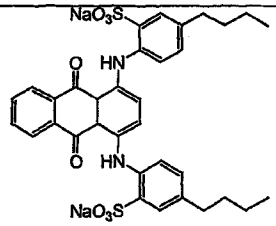
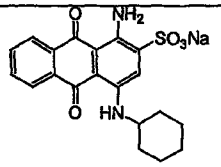
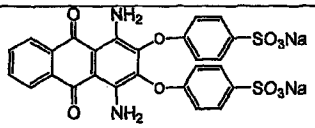
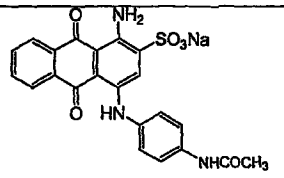
A transition metal catalyst may also be used in the absence of peroxyl species where the bleaching is termed to be via atmospheric oxygen, see, for example WO02/48301. Photobleaches, including singlet oxygen photobleaches, may be used with the laundry treatment composition. A preferred photobleach is vitamin K.

Experimental

Example 1 - Dye substantivity

To determine the substantivity of a range of dyes the following experiment was performed. A stock solution of 1.5g/L of a base washing powder in water was created. The washing powder contained 18% NaLAS, 73% salts (silicate, sodium tri-poly-phosphate, sulphate, carbonate), 3% minors including perborate, fluorescer and enzymes, remainder impurities and water. The solution was divided into 60ml aliquots and dye added to this to give a solution of optical density of approximately 1 (5 cm pathlength) at the maximum absorption of the dye in the visible lengths, 400-700nm. The optical density was measured using a UV-visible spectrometer. One piece of bleached, non-mercerised, non-fluorescent woven cotton cloth (ex Phoenic Calico) weighing 1.3g was placed in the solution at room temperature (20°C). This cloth represents a slightly yellow cotton. The cloth was left to soak for 45 minutes then the solution agitated for 10 mins, rinsed and dried. Following this the optical density of the solution was re-measured and the amount of dye absorbed by the cloth calculated. This experiment was repeated for each dye and the results provided in the table below. A cotton substantive dye is one which has a deposition greater than 8 % per the above test.

Dye and structure	% Deposition
 Acid Black 1 - an azo dye	22
 Acid blue 113 - an azo dye	26
 Acid violet 17 - a triphenyl methane dye	18
 Direct Violet 51 - an azo dye	69
 Direct Blue 71 - an azo dye	34
 Acid blue 45 - an anthraquinone dye	8

 Acid Blue 80 - an anthraquinone dye	0
 Acid blue 25 - an anthraquinone dye	29
 Acid green 27 - an anthraquinone dye	4
Acid blue 205 - an anthraquinone dye	14.6
 Acid blue 62 - an anthraquinone dye	27.8
Acid blue 281 - an anthraquinone dye	23.2
 Acid violet 42 - an anthraquinone dye	7.4
 Acid blue 40 - an anthraquinone dye	45.3

Acid blue 290 - an anthraquinone dye	12.5
Acid blue 264 - an anthraquinone dye	14.8
Acid blue 221 - an anthraquinone dye	5.8
Acid blue 171 - an anthraquinone dye	19.9
Acid blue 204 - an anthraquinone dye	4.8
Acid blue 225 - an anthraquinone dye	13.0

A wide range of dyes may deposit to cotton. Within the anthraquinone dyes acid blue 25, 205, 62, 281, 40, 290, 264, 171 and 225 shows a high level (>10%) of deposition. The highest level of deposition (>20%), and hence the most efficient at colouring the cloth were acid blue 25, 62, 281 and 40.

Example 2: Deposition on Nylon

The experiment of example 1 was repeated for the anthraquinone dyes listed below, but nylon was used as the fabric.

Dye	% Deposition
Acid blue 25- an anthraquinone dye	14.5
Acid blue 205 - an anthraquinone dye	15.7
Acid blue 62 - an anthraquinone dye	13.1
Acid blue 281 - an anthraquinone dye	22.4
Acid violet 42 - an anthraquinone dye	4.7
Acid blue 40 - an anthraquinone dye	12.8
Acid blue 290 - an anthraquinone dye	6.2
Acid blue 264 - an anthraquinone dye	17.8
Acid blue 221 - an anthraquinone dye	3.1
Acid blue 171 - an anthraquinone dye	43.7

Acid blue 204 - an anthraquinone dye	5.0
Acid blue 225 - an anthraquinone dye	8.0

Acid dyes which deposit to nylon in the wash build up on the nylon over multiple washes and can overshade this fabric, as discussed in WO 2005/003275. It is therefore preferred that the deposition to nylon is much smaller than cotton, preferable at least 50% lower. Preferred dyes are those which have much lower deposition on nylon to cotton. Acid anthraquinone dyes are widely used to dye nylon but not cotton articles, and therefore would not be expected to have this characteristic. However surprisingly the data shows that acid blue acid blue 25, 62, 40 and 290, do have this property whilst showing good deposition to cotton.

Example 3 - Dye Photofading

Non-mercerised cotton cloth was dyed with the dyes listed in the table below. The dying was done from a wash solution containing the washing powder described in example 1 with dye added to solution to give a similar level of colour on the cloth (measured as the Delta E value relative to undyed cloth). Following the dying the photostability of the dyes on cotton was investigated by irradiating the cloth for 5 hours in a weatherometer set to give 385 W/m^2 in the UV-visible range. The Delta E of the cloth was then remeasured, if the value had greatly dropped then the dye has been substantially photofaded.

Dye	Initial Delta E	Delta E after 5 hour irradiation
Acid blue 25	14.0	13.2
Acid blue 62	13.2	11.2
Acid blue 281	15.1	12.3
Acid blue 40	17.9	17.9
Acid blue 264	13.4	12.0
Acid black 113	13.4	9.0
Acid Black 1	10.6	7.3
Acid Violet 17	10.5	3.2

The anthraquinone dye have a superior photostability on cotton than the azo or triphenylmethane dyes.

We Claim:

1. A laundry treatment composition comprising from 2 to 60 wt % of a surfactant and from 0.0001 to 0.02 wt % of a dye selected from acid blue 62, 40 and 290.

2. A laundry treatment composition according to claim 1, wherein the dye is acid blue 62.

3. A laundry treatment composition according to claim 1 or 2, wherein the laundry treatment composition is a detergent washing composition.

4. A method of treating a textile, the method comprising treating the textile with an aqueous solution of an dye selected from acid blue 62, 40 and 290, wherein the dye is present in solution at a concentration in the range from 10 ppb to 1 ppm.

5. A method of treating a textile according to claim 4, wherein the ionic strength of the solution is in the range from 0.001 to 0.5.

6. A method according to claim 4 or 5, wherein the aqueous solution has a pH in the range from 7 to 12 and a surfactant is present at a level in the range from 0.1 g/L to 4g/L.

7. A method according to claim 6, wherein the aqueous solution has a pH in the range from 8 to 11 and the surfactant is present at a level in the range from 0.25 to 2.5g/L.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 198305 Derwent Publications Ltd., London, GB; Class A97, AN 1983-10625K XP002384512 & JP 57 205500 A (LION CORP) 16 December 1982 (1982-12-16) abstract	1-7
A	WO 2005/003275 A (UNILEVER NV UNILEVER PLC HINDUSTAN LEVER LTD) 13 January 2005 (2005-01-13) cited in the application claims; examples	1-7

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 June 2006	22/06/2006

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Pfannenstein, H

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/002300

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 2006/032397 A (HINDUSTAN LEVER LTD UNILEVER NV UNILEVER PLC) 30 March 2006 (2006-03-30) page 7; claims	1-7
X	GB 2 145 729 A (LION CORP) 3 April 1985 (1985-04-03) claims	1-7

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2006/002300

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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WO 2005003275 A	13-01-2005	CA 2529726 A1	13-01-2005
		EP 1633843 A1	15-03-2006
WO 2006032397 A	30-03-2006	NONE	
GB 2145729 A	03-04-1985	JP 1344946 C	29-10-1986
		JP 60051798 A	23-03-1985
		JP 61011995 B	05-04-1986